Chapter 3
Role of Nanostructured Materials Toward Remediation of Heavy Metals/Metalloids

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Abstract In recent scenarios, the development of nanotechnology with novel size, shape, and surface dependent properties has revealed incredible prospective for the treatment of environmental problems especially toxic heavy metals from contaminated water. As compared with traditional materials, a nanosized particle exhibits to a large extent efficiency and faster remediation rates in water treatment. Many kinds of nanomaterials such as carbon, nanometal/metal oxides, and polymer based have high selectivity and adsorption potential for the remediation of heavy metals/metalloids such as As^{5+}, As^{3+}, Pb^{2+}, Cr^{3+}, Cr^{6+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} from contaminated water. This chapter gives a widespread analysis on the enduring research and progress activities in the field of remediation of toxic heavy metals/metalloids from contaminated water by using nanomaterials in order to achieve environmental detoxification, using adsorption process. We have also discussed the essential aspects of heavy metals problems on environment; their effects on human health through polluted water are reviewed.

Keywords Water pollution · Toxicity · Heavy metals/metalloids
Nanomaterials · Adsorption

3.1 Introduction

Water is the most valuable substance on this earth. All the life entities need water to survive. Without water then there would be no life on the earth. Drinking water quality is a common concern for people all over the world. We can survive days or

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even weeks without food, but cannot survive for long without water. Water quantity and quality is an important issue for public health. It is a well-known fact that clean drinking water is absolutely essential for healthy living. Water covered 326 million cubic miles on the Earth; however, only 3/10,000 is fresh water that can use for bathing, washing, cooking, and drinking. The rest percent is sheltered in oceans, icecaps glaciers, atmosphere, and ground water. But this 3% of water is also getting polluted by human deeds.

The contagion of water bodies such as oceans, rivers, aquifers, lakes, oceans, and groundwater is called water pollution. This water pollution occurs when pollutants are directly or indirectly discharged into natural water without proper treatment. Water pollution not only affects plants and animals but also affect the aquatic life. Approximately, the effect of water pollution is dangerous not only to human beings but also to the entire biosphere communities [1–3]. The problem of water pollution becoming severe day by day due to increase in population and increasing industrial activities. Many areas of surface water and groundwater are now contaminated with pathogens, harmful chemicals, and toxic heavy metals. Worldwide diseases like cancer, congenital malformation, and endocrine disturbances are associated with the contaminated drinking water.

Heavy metal toxicity is one of the leading problems in the current industrialized era. Wastewater from numerous industries, tanneries, battery manufacturing, metallurgical activities, electroplating, chemical manufacturing, and mining industries hold huge quantity of heavy metal ions [4, 5]. These wastewaters are discharged into water bodies directly, threatening not only the aquatic organisms, but also harming human and animals through their food chain. In numerous parts of the world, heavy metal concentration in drinking water is higher than the international guidelines values provided by the World Health Organization (WHO) and Bureau of Indian Standard (BIS).

Heavy metal is defining by the density of the metals in most of the cases. It is, thus, defined as those metals having a specific density in excess of 5 g/cm^3 and toxic even in low concentration in contact with water and can have lethal effect on human bodies [6, 7]. It has been reported that about 1.6 million children die every year by consuming contaminated water. In the country like India, 80% of people are dying because of drinking toxic heavy metal contaminated water [6, 7]. The effects of these metals on human health are regularly reviewed by global bodies such as the World Health Organization [WHO]. Thus, the elimination of heavy metal ions from water bodies is vital to safeguard the environment and public health. To improve the quality of drinking water, the development of sustainable and robust technologies, chips, etc., has become of fundamental importance.

Several methods have been introduced to eradicate heavy metal ions from water such as chemical precipitation [8], membrane filtration [9], ion exchange [10], reverse osmosis [11], extraction [12], electrochemical treatment techniques [13], irradiation [14], coagulation [15], and adsorption [16]. But adsorption [17] shows most potential method to eliminate heavy metal ions from water as compared to others due to being inexpensive and extremely flexible. Carbon, zeolites, clay minerals, and chitosan have been explored for the adsorption of heavy metals by numerous researchers but the less adsorption ability and elimination competence restricts its application.

Current advancement in nanotechnology provides a hopeful way to resolve the environmental problems and offers protective dealings for future problems resulting from the exchanges of energy and resources with the environment [18, 19]. The most important environmental applications of nanotechnology could be elimination of toxic heavy metals ions from polluted water.

The major demerits of traditional sorbents in removal of heavy metals from wastewater could be solved by nanostructured materials. These nanomaterials have size ranging from 1 to 100 nm. As compared with traditional materials, nanomaterials show advanced effectiveness and quicker adsorption rates of heavy metals due to its novel size, large surface area, and shape dependent properties resulting in high reactivity to various heavy metals ions.

3.2 Heavy Metals/Metalloids and Their Sources

Water pollution caused by hazardous heavy metals and metalloids can occur from both natural as well as anthropogenic sources [20, 21]. Commonly known natural sources of heavy metals are mainly volcanic activities, rocks, ore minerals that are hidden in the crust, forest fires, etc., [21]. Anthropogenic sources of heavy metals pollution are increasing due to industrial waste, use of fertilizers, pesticides, sewage sludge, mining, combustion of coal and other fossil fuels. The toxic waste occurs due to both industrial production and end-used products landing into water bodies. Many industries like metal smelting, leather tanning, semiconductor, chemical manufacturing, etc., directly discharge heavy metal ions contaminated wastewater into natural water without adequate treatment [20, 21]. Thus, industrialized countries are more often faced with the impact of toxic heavy metals. Table 3.1 provides the anthropogenic sources of heavy metal pollutants provided by Dr. Gautam SP, CPCB New Delhi [22].

As discussed above about the sources of pollution by toxic heavy metals into the environment, mining is yet another such major source. There are many reports in this regard. For example, the effluents released in water bodies from Zawar mines in Udaipur district found to have higher levels of hazardous zinc and lead [23] causing toxicity of water. In another study by Shulka [24] of the water samples of northeast coalfield region of Chhattisgarh, it was found that level of cadmium, lead, iron, zinc, chromium, copper in the water was beyond the permissible limit. Hu et al. [25] have reported extensively in their study on the pollution of heavy metals in China. Their study suggests mining is one of the prime reasons of the heavy metal pollution in China. In gold mining, mercury (Hg) is used for amalgamation of gold. Most of the mercury is removed in this process and reused; however, some of the mercury enters in the river system. The gold mining activity is prime reason for the Amazon basin system to pollute [26].

Table 3.1 Sources of heavy metals (*Source* provided by Gautam SP, CPCB New Delhi)

Metals	Industries
Chromium (Cr)	Mining, industrial coolants, chromium salts, manufacturing, leather tanning
Lead (Pb)	Lead acid batteries, paints, E-waste, Smelting operations, coal based thermal power plants, ceramics, bangle industry
Mercury (Hg)	Chlor-alkali plants, thermal power plants, fluorescent lamps, hospital waste (damaged thermometers, barometers, sphygmomanometers), electrical appliances etc.
Arsenic (As)	Geogenic/natural processes, smelting operations, thermal power plants, fuel burning
Copper (Cu)	Mining, electroplating, smelting operations
Cadmium (Cd)	Zinc smelting, waste batteries, e-waste, paint sludge, incinerations & fuel combustion
Molybdenum (Mo)	Spent catalyst
Zinc (Zn)	Smelting, electroplating
Nickel (Ni)	Smelting operations, thermal power plants, battery industry
Vanadium (Va)	Spent catalyst, sulphuric acid plant

Since ages, the agriculture has remained a prime economic activity for human beings to survive. Because of the ever increasing population, the demand for food is increasing at rapid rate, therefore, need to produce more is need of hour. In order to produce more, the increase in use of fertilizers and pesticides have taken place. For healthy growth of crops, heavy metals like Cu, Zn, Mo, Ni, Fe, Mn, and Co are also essential apart from macronutrient like N, P, K, etc. The compounds via which these elements are supplied also contain some amount of Cd and Pb, which upon prolonged use are deposited in the soil [27]. These metals enter the ground water via interconnection between soil and groundwater and hence causing water pollution [26].

Biosolid waste is another source of heavy metal contamination to the soil and hence the groundwater and water bodies. Biosolids like livestock manure, sewage sludge, etc., contain heavy metals such as Sb, Cr, Cd, and As. When these solids are used over the land in the activities such as agriculture, then over a period of time they could accumulate and hence may contaminate water [23].

3.3 Effects of Heavy Metals/Metalloid in Human Health

Heavy metals are very dangerous for both human health and aquatic life, if, it crosses the maximum permissible limit because heavy metals are inclined to bioaccumulate [28]. Bioaccumulation indicates an increase of a chemical in living bodies eventually, compared to the concentration of chemicals in the environment [28]. Accumulation of heavy metals in living things is faster in rate than the substance is lost by catabolism and excretion. Five most common heavy metals that are very toxic to both human and aquatic life even at low concentration and reviewed by WHO many times which are discussed in brief are: lead, cadmium, chromium, mercury, and arsenic [29, 30]. Severe exposures to heavy metals have been known and it continues to grow unabated in many parts of the world. Particularly, the exposure is increasing in less developed countries like Pakistan, India, and Bangladesh [22]. Too much of heavy metal consumption can damage different systems of the body together with the reproductive system, nervous, kidneys and it can cause cancer, high blood pressure, and anemia [30, 31]. The symptoms consist of headache, abdominal pain, irritability, confusion, and in severe cases it can cause coma, seizures, and death [5, 31, 32].

Arsenic is classified as a heavy metal but it is actually a metalloid. It is abundant in our environment with both natural and anthropogenic sources [33, 34]. In water, arsenic has leading forms of inorganic species such as arsenate [As^{5+}] and arsenite [As^{3+}] [33, 34]. Maximum permissible limit of arsenic in drinking water set by the WHO and BIS is at 0.01 mg/L [35, 36]. Arsenic consumption is mostly due to intake of seafood and drinking water. Its long-standing exposure enhances risk of skin cancer, lesions, hyperkeratosis, and pigmentation changes [37, 38]. Results show occasional exposure to arsenic can have risk of lung cancer [38].

Lead is a poisonous heavy metal that is dangerous to human health. In contact with water, lead is colorless, odorless, and tasteless. In drinking water, the maximum permissible limit of lead set by the WHO and the BIS is 0.01 mg/L [35, 36]. In child, the high level of lead exposure can result with neurological damage, coma, organ failure, and ultimately death [39]. The exposure in low level can affect learning disabilities; inhibit growth, and hearing loss [31, 39]. The symptoms show poor appetite, vomiting, sleep disorder, cramps, irritability, fatigue, and constipation [39]. It can easily accumulate within the body for a long time, i.e., bioaccumulate [21], which possibly is stored in the kidney, bones, brain, and other main organs. Lead can also store in the blood and bones of child's for several decades [31, 39].

Mercury is exceptionally toxic heavy metals and it must be handled properly. The permissible limit of mercury in drinking water set by the WHO and the BIS is at 0.006 mg/L and 0.001 mg/L, respectively [35, 36]. The exposure of mercury can harm the nervous system, impair hearing, speech, vision and gait, involuntary muscle movements, corrodes skin, and mucous membranes. It can also cause the problem of chewing and swallowing of food [40]. In India, the general population is exposed to mercury due to intake of seafood and drinking contaminated water [41]. The pregnant women need to avoid a high intake of seafood, such as fish, shark, tuna, and swordfish, taken from polluted waters [40].

The maximum permissible limit of **cadmium** in drinking water set by the WHO and BIS is at 0.003 mg/L [35, 36]. It was first reported in Japan that extended exposure of cadmium might give rise to dangerous bone disease, called itai-itai ("ouch-ouch"). It was first reported from the Jinzu river basin in Japan [29, 31]. Cadmium exposure can also lead to harmful effects such as renal damage, emphysema, chronic disorders, and skeletal malformation in fetus, hypertension, kidney damage, and testicular atrophy [29]. Cadmium is also considered as carcinogenic reported by the International Agency for Research on Cancer (IARC, 1993). The IARC's study was based on occupationally exposed workers [31]. In India, many people have already exceeding cadmium exposure levels, and the edge is very thin. Therefore, proper treatment should be taken to decrease the cadmium hazard to diminish the unpleasant health effects.

In contact with water, **chromium** forms two stable oxidation states, Cr^{3+} and Cr^{6+} [42]. Cr^{6+} is far more poisonous than Cr^{3+} to living things for its carcinogenicity, toxicity, and high aqueous solubility. Currently, the WHO has set a permissible limit for chromium in drinking water at 0.1 mg/L and the BIS at 0.05 mg/L [35, 36]. The exposures to Cr^{6+} occasionally raises the risk of cancers in the respiratory system. Zhang and Li [43] recently reported that in China (resident in the Liaoning), the death due to stomach cancers increased. The reasons behind this are drinking water in resident Liaoning was greatly contaminated with Cr^{6+} which are released by the ore smelting industries.

Copper is a reddish metal and is a crucial element for all the living organisms. It is vital in diet to assure good health. On the other hand, too much absorption of copper can be root of adverse health effects, including stomach cramps, nausea, vomiting, diarrhea, etc., [44]. It has also been reported that too much exposure of copper can cause liver and kidney damage [31]. In drinking water, the maximum permissible limit of copper set by the WHO is at 2 mg/L and by the BIS is at 0.05 mg/L [35, 36]. Therefore, removal of these heavy metals is very necessary for clean and healthy environment. Table 3.2 provides the maximum permissible limits of heavy metals set by the WHO and BIS in drinking water (Sources provided by the WHO and BIS). Figure 3.1 shows the six hazardous heavy metals in drinking water.

Table 3.2 Maximum permissible limit of heavy metal in drinking water by WHO and BIS

Sl. No.	Heavy metal/metalloids	World Health Organization (WHO) (mg/L)	Bureau of Indian Standards (BIS) (mg/L)
1	Arsenic (As)	0.01	0.01
2	Lead (Pb)	0.01	0.01
3	Chromium (Cr)	0.1	0.05
4	Cadmium (Cd)	0.003	0.003
5	Copper (Cu)	2	0.05
6	Mercury (Hg)	0.006	0.001
7	Zinc (Zn)	5	5
8	Nickel (Ni)	0.07	0.02
9	Molybdenum (Mo)	0.07	0.07
10	Selenium	0.01	0.01
11	Uranium	0.015	–
12	Barium	0.7	0.7
13	Silver	0.1	0.1

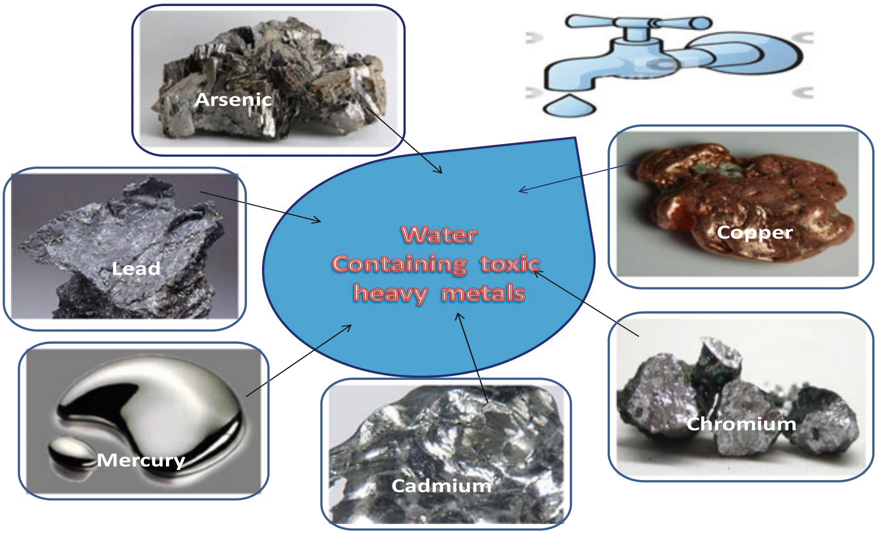

Fig. 3.1 Drinking water contains heavy metals

3.4 Nanomaterials as Adsorbent for Heavy Metals/Metalloids

Nanomaterials as sorbents for elimination of heavy metals/metalloids ions from wastewater should have following criteria. The nanosorbents should be nontoxic and have high sorption capacities. The adsorbed metal ions could be detached easily from the surface of the nanoadsorbents and could be infinitely recycled [29]. So far, a varieties of nanomaterials such as carbon, metal and metal oxides, and polymer supported nanoadsorbents have been studied for the removal of heavy metal from water, and the results indicate that highest explored nanoadsorbents were carbon, nanozero-valent iron and iron oxide-based nanoadsorbents due to their large surface area volume ratio, low cost, easy availability, nontoxic, and recyclable [29, 45]. Few metal oxide nanoadsorbents such as TiO_2, CeO, MnO, and AlO were also explored for the removal of heavy metals from water [46]. Polymer supported nanoadsorbents have also been explored by the researcher in this field [47]. Figure 3.2 shows the pie chart of explored utilization of different nanomaterials as sorbents for heavy metal remediation from water.

3.4.1 Carbon-Based Nanomaterials

Undoubtedly, carbon-based nanomaterials are the most admired and broadly used adsorbent for the applications in wastewater treatment all over the world. In recent

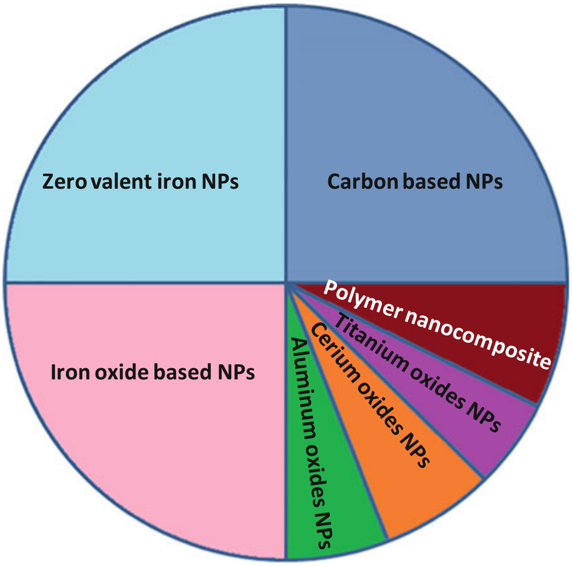

Fig. 3.2 Pie chart of explored utilization of different nanomaterials absorbents for heavy metal remediation from water

decades, carbon-based adsorbent [48] is extensively used for the removal of heavy metals from waste water due to its nontoxic, low-cost, and high sorption capacities [6]. Firstly, activated carbon was used as sorbents for heavy metal remediation but have demerits to remove heavy metals at ppm [parts per million (mg/L)] level [6]. To overcome these demerits, nanotechnology recently designs graphene, carbon nanotubes, and fullerene used as nanosorbents for the remediation of heavy metals [6, 48].

Lijima was the first who discovered carbon nanotubes (CNTs). Owing to their exclusive structural, mechanical, optoelectronic, semiconducting, electronic, chemical, and physical properties, CNTs have been used extensively to eliminate heavy metals from wastewater [6]. CNTs have two forms, single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Many studies have revealed that CNTs have outstanding adsorption capacity and have high adsorption effectiveness for various heavy metals as compared with other adsorbent [49, 50]. Li et al. [49] have reported CTNs have excellent adsorption capacity for Pb^{2+} from water. Li et al. [50] again reported thermodynamics studies of Pb^{2+} adsorption on carbon nanotubes in a range of temperatures; 280, 298, and 321 K and calculate all the thermodynamic constant such as equilibrium constant, standard entropy change, and standard-free energy. The desorption result also reveals that Pb^{2+} can be removed easily from CNTs by varying the solution pH using HNO_3 and HCl, which signifies that CNTs can be reused again. Hu et al. [51] reported chromium removal using oxidized MWCNTs. The result indicates that chromium adsorption mostly depends on the redox reaction of Cr^{6+} ions on the surface of oxidized MWCNTs to form Cr^{3+}, and ensuing Cr^{3+} sorption on MWCNTs appears as the foremost mechanism for the uptake of chromium on MWCNTs.

Pillay et al. [52] reported the adsorption capabilities of Cr^{6+} using three carbon-based adsorbents that are: activated carbon, functionalized MWCNTs, and unfunctionalized MWCNTs. The results revealed that unfunctionalized MWCNTs showed the highest adsorption capability with up to 98% out of 100 mg/L of Cr^{6+} solution being adsorbed. Pyrzyńska and Bystrzejewski [53] reported comparative study of heavy metals ion Co^{2+} and Cu^{2+} adsorption onto activated carbon, carbon nanotubes, and carbon-encapsulated magnetic nanoparticles. The results indicate CNTs have less sorption capacity as compared with carbon nanomaterials. In the meantime, Stafiej and Pyrzynska [54] reported solution pH, including metal ions concentrations, could affect the adsorption distinctiveness of CNTs, and the experimental data agreed well with the Freundlich adsorption isotherm model. Kosa et al. [55] reported modified carbon nanotubes with 8-hydroxyquinoline and used it for the removal of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}. The results revealed that the modification of CNTs with 8-hydroxyquinoline improved the removal efficiency of heavy metals.

Graphene is an additional parts of carbon nanomaterials, having one or more atomic layered graphite. It has two-dimensional structure having excellent thermal and mechanical properties. Zhao et al. [56] reported synthesis of few-layered graphene oxide nanosheets using modified Hummers method and used these graphene nanosheets as sorbents for the elimination of Cd^{2+} and Co^{2+} ions from water. The results signify that sorption of heavy metal on graphene nanosheets is dependent on solution pH, ionic strength, and the abundant oxygen-containing functional groups on the surfaces of graphene oxide nanosheets. Zhang et al. [57] reported composites graphene oxide/magnetite (GO/Fe_3O_4) synthesized via a copper catalyzed azide-alkyne cyclo addition reaction. Further, GO/Fe_3O_4 was modified with polyacrylic acid (PAA) to obtain PAA/GO/Fe_3O_4 which was used for the removal of Cu^{2+}, $Cd^{2+,}$ and Pb^{2+} ions from water. It is found that the PAA/GO/Fe_3O_4 nanocomposite shows extraordinary removal effectiveness for Cu^{2+}, $Cd^{2+,}$ and Pb^{2+} ions. Chandra et al. [58] reported a size of 10 nm magnetite-graphene adsorbents for the removal of As^{3+} and As^{5+} from water. The outcome signifies the high uptake of arsenic as a result of the increased adsorption sites in composite of graphene. Yang et al. [59] reported aggregation of Graphene oxide (GO) by Cu^{2+} in aqueous solution, indicates enormous Cu^{2+} absorption capacity. The study characterized by atomic force microscopy and confocal microscopy reported that Cu^{2+} ions folded GO sheets and creates large aggregation along with increased adsorption sites. The results demonstrate 10 times adsorption capacity then activated carbon. Table 3.3 shows the carbon-based nanoadsorbents explored for the remediation of heavy metals from water. Figure 3.3 shows the different shapes of carbon-based nanoadsorbents.

3.4.2 Nanosized Metal and Metal Oxides

Recently, metal and metal oxide nanoadsorbents (NMO) such as nanosized zero-valent iron (NZVI), ferric oxides, titanium oxides, cerium oxides, manganese

Table 3.3 Carbon-based nanoadsorbents used for heavy metal remediation

Carbon-based nanoadsorbents	Heavy metal	References
CNTs	Pb^{2+}	[49]
CNTs	Pb^{2+}	[50]
Oxidized MWCNTs	Cr^{6+}, Cr^{3+}	[51]
MWCNTs	Cr^{6+}	[52]
Activated carbon, CNTs, and carbon-encapsulated Fe_3O_4	Co^{2+}, Cu^{2+}	[53]
CNTs	Cu, Co, Cd, Zn, Mn, Pb	[54]
MWCNTs modified 8-hydroxy quinoline	Cu^{2+}, Pb^{2+}, Cd^{2+}, Zu^{2+}	[55]

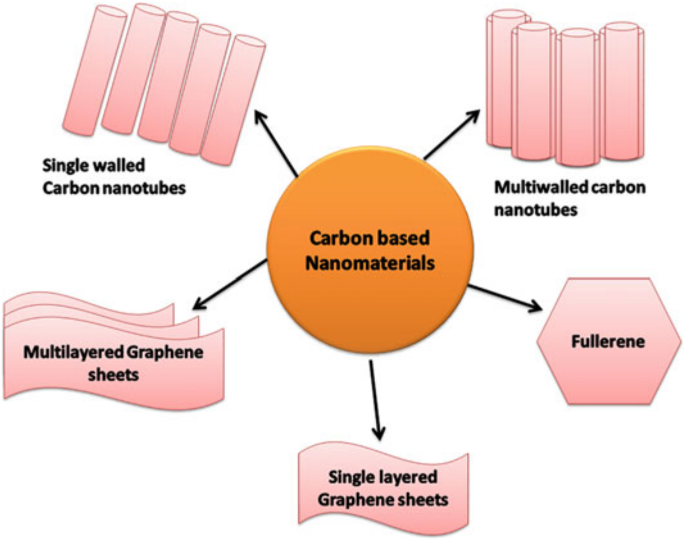

Fig. 3.3 Different shapes of carbon-based nanomaterials

oxides, aluminum oxides were explored as the most gifted adsorbent for the remediation of heavy metals from water [45, 46, 60–64]. The motivation behind this is due to their large surface areas and high adsorption capacity caused by the size-quantization effect [65, 66]. The study reported that NMOs show evidence of very favorable sorption to heavy metals in terms of high capacity and selectivity. On the other hand, the surface energy increases as the size of NMOs decreases from micrometer to nanometer levels, which reduces their stability. Therefore, NMOs can easily aggregate due to Van der Waals forces and other interactions [66], which very much decreases the high adsorption capacity and selectivity of NMOs. Additionally, NMOs have poor mechanical strength and too much pressure drops which leads to unfeasible in fixed beds. To overcome this all problems, many researchers have impregnated NMOs into porous supports to obtain composite nanoadsorbents [47], which include amino acids, polymers, activated carbon, natural materials, etc. Above and beyond as compared with all traditional NMOs, magnetic nanoadsorbents create a center of attention because of their large surface area, ecofriendly, availability, low cost and it can be simply separated from water applying magnetic field [60, 61]. Furthermore, magnetic composite adsorbents can easily be regenerated or recycled [61], which reduces the cost of wastewater management (Fig. 3.3).

3.4.2.1 Iron-Based Nanoparticles as Nanoadsorbents for Heavy Metals

The exploitation of iron-based nanoadsorbents have been acknowledged to a great extent in the field of heavy metals remediation from water due to their exceptional properties, for instance small size, high surface area to volume ratio, ecofriendly, excellent magnetic properties, and great ability of surface modification.

Zero-Valent Iron: Among all the metal/metal oxide nanomaterials, nanoscale zero-valent iron (NZVI) has distinguished itself by its unique properties that include low cost, low toxicity, ecofriendly, larger surface to volume ratio, diminish the chemicals consumption, no secondary pollutant, strong adsorption ability, and easy separation under external magnetic field [60, 67]. Therefore, these properties make NZVI as the excellent adsorbent for the treatment of heavy metals from water. Ponder et al. [67] reported quick removal of Cr^{6+} and Pb^{2+} from aqueous solution using supported NZVI (“Ferragels”). The result indicates supported NZVI, while oxidizing the Fe to goethite (R-FeOOH) reduced the Cr to Cr^{3+} and the Pb to Pb^0. Kanel et al. [33, 34] reported that NZVI rapidly removes As^{3+} and As^{5+} from groundwater. The maximum adsorption capacity of As^{3+} obtained from Freundlich adsorption model was 3.5 mg/g. Boparai et al. [68] investigated NZVI for the removal of Cd^{2+} (conc. range 25–450 mg/L). The results recommend the competent removal of Cd^{2+} from contaminated water. Zhang et al. [69] reported that NZVI has limitation to remediate contaminated groundwater due to lack of durability and mechanical strength. To overcome these problems, NZVI was loaded onto kaolinite as a support material (K-NZVI) and used for the remediation of Pb^{2+} from water. The results show 96% of Pb^{2+} was removed within 30 min using 10 g/L K-NZVI in 500 mg/L Pb^{2+}. Kim et al. [70] reported the Zeolite supported NZVI for the removal of Pb^{2+} from aqueous water and the results designated immense potential of Pb^{2+} elimination from water. Su et al. [71] reported the removal of NZVI to the co-contaminants Cd^{2+} and nitrates. The result indicates increase in solution pH and negative charge of NZVI increases the removal of Cd^{2+} from 40 to 188 mg/g with nitrate present and 30% of nitrate was reduced by NZVI within 2 h. Liu et al. [43] reported NZVI supported on pumice (P-NZVI) successfully removed Hg^{2+} and Cr^{6+} from wastewater. The maximum uptake of Hg^{2+} and Cr^{6+} onto P-NZVI was 332.4 and 306.6 mg/g, respectively. Table 3.4 shows the NZVI adsorbents for the removal of heavy metals from water.

Iron Oxide-based nanoadsorbents exist in various forms in nature such as Goethite (γ-FeOOH), Maghemite (γ-Fe_2O_3), Hematite (α-Fe_2O_3), and Magnetite (Fe_3O_4) [72]. Recently, the majority of research for the applications of wastewater

Table 3.4 Zero-valent iron NPs for the removal of heavy metals

Zero-valent iron nanoadsorbents	Heavy metals	References
NZVI	Pb^{2+}, Cr^{6+}	[67]
NZVI	As^{5+}	[33]
NZVI	As^{3+}	[34]
(K-NZVI)	Pb^{2+}	[69]
Zeolite/NZVI	Pb^{2+}	[70]
NZVI	Cd^{2+}	[68]
NZVI	Cd^{2+}	[71]
P-NZVI	Hg^{2+}, Cr^{6+}	[43]

treatment has focused on iron oxide nanoadsorbents [72, 73]. Nasser [73] reported the maximum adsorption capacity for Pb^{2+} ions was obtained as 36.0 mg/g by Fe_3O_4 NPs, which was much higher than that of reported low-cost adsorbents. The small size of Fe_3O_4 NPs was favorable for the diffusion of metal ions from solution on to the active sites of the adsorbents surface. The result indicates that Fe_3O_4 nanosorbents were effective and economical adsorbents for rapid removal and recovery of metal ions from wastewater effluents. Sarkar and Sarkar [74] investigated the applicability of polyethylene glycol (PEG-4000) coated Fe_3O_4 magnetic nanoparticles for the selective removal of toxic Pb^{2+} ion from wastewater. The result indicates maximum adsorption of Pb^{2+} at optimum pH 6, and the equilibrium contact time is 10 min. Wang et al. [75] reported synthesized water-soluble Fe_3O_4 NPs through a hydrothermal method and found excellent removal of Pb^{2+} and Cr^{6+} ions from waste water. The result indicates more than 90% of Pb^{2+} and Cr^{6+} ions were removed within 2 min.

Xin et al. [76] reported amine-functionalized mesoporous Fe_3O_4 NPs (AF-Fe_3O_4) used for the removal of Pb^{2+}, Cd^{2+}, and Cu^{2+} ions from water. The result indicates the adsorption of these heavy metals agreed well with Langmuir isotherm model and the maximum adsorption capacities for Pb^{2+}, Cd^{2+}, and Cu^{2+} from 369.0 to 523.6 mg/g, which is superior to other reported work. Liu et al. [77] reported Humic acid (HA) coated Fe_3O_4 NPs (Fe_3O_4/HA) successfully removed toxic heavy metals Hg^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} from water. The maximum removal efficiency of the heavy metals reached equilibrium within 15 min, and agreed well with Langmuir isotherm adsorption with maximum uptake from 46.3 to 97.7 mg/g. The result indicates 99% removal of Hg^{2+}, Pb^{2+}, and almost 95% of Cd^{2+}, and Cu^{2+}. Bagbi et al. [78] reported monodispersed Fe_3O_4 NPs synthesized by chemical co-precipitation and used for successful removal of Pb^{2+} from water (Fig. 3.4). The result indicated 100% removal of Pb^{2+} within 30 min. Pseudo-second-order rate equation shows better fitted data. Spent Fe_3O_4 NPs were regenerated using 0.005 M HNO_3. Grossl et al. [79] investigate Cu^{2+} adsorption/desorption studies using goethite (a-FeOOH) NPs applying pressure-jump relaxation technique. The relaxations rate of Cu^{2+} decreased with an increase in pH. The results indicate that the rate of adsorption of divalent metal cations on goethite was directly related to the rate of removal of a water molecule from the primary hydration sphere of a

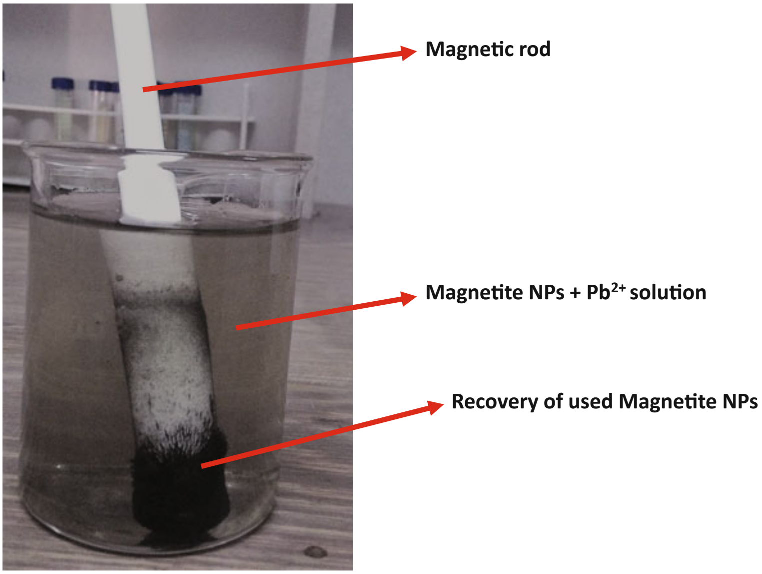

Fig. 3.4 Demonstration of manipulating magnetite NPs using a simple magnet [78]

particular divalent metal cation. Chen et al. used Goethite and hematite nanoadsorbents for the removal of Cu^{2+}. It was reported that both the nanoadsorbents show high adsorption uptake of Cu^{2+} [80]. The obtained maximum adsorption capacity of Cu^{2+} is 149.25 and 84.46 mg/g for goethite and hematite nanoadsorbents, respectively. It also indicates that adsorption of Cu^{2+} was fitted well with Langmuir adsorption isotherm as compared with Freundlich model. Hu et al. [81] investigated maghemite NPs for the removal of Cr^{6+} from waste water. The removal of heavy metal was very fast and within 15 min adsorption equilibrium reached. The adsorption data were analyzed and fitted well by Freundlich isotherm. Cr^{6+} adsorption capacity of maghemite nanoparticles was compared favorably with other adsorbents like activated carbon and clay. Regeneration studies of maghemite underwent six successive adsorption desorption processes. Hu et al. [82] reported the applicability of maghemite (γ-Fe_2O_3) NPs for the removal of Cr^{6+}, Cu^{2+}, and Ni^{2+} from electroplating wastewater. The result indicated adsorption of heavy metals reached equilibrium rapidly within 10 min and Langmuir adsorption isotherm fitted well. Regeneration studies of γ-Fe_2O_3 NPs adsorption desorption processes undergo successfully retained metal removal capacity.

3.4.2.2 Nanosized Titanium Oxides

Titanium dioxide (TiO_2) was recently explored as the adsorbent for the application of heavy metals remediation from water. It has three different crystal structures such as anatase, rutile, and brookite. The brookite type cannot be used in industries due to its low stability at room temperature and rutile type is easily coagulated at room temperature and its band gap energy is larger than that of anatase type [83]. Therefore, anatase-type TiO_2 used as an adsorbent to investigate the photo adsorption effect was selected. It was reported that bulk and nanoparticle TiO_2 anatase exhibit different chemical behavior, catalytic reactivity, and surface acidity based on their different surface planes [83, 84]. Engates and Shipley [45] investigated adsorption of metals (Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}) using TiO_2 nanoparticles and bulk particles. The result indicates successful removal of multiple metals (Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}) at solution pH 8 and spiked San Antonio tap water.

Liang et al. [85] investigated new method using TiO_2 nanoadsorbents as solid-phase extractant coupled with Flame atomic absorption spectrometry (FAAS) was proposed for preconcentration and determination of trace Zn^{2+} and Cd^{2+}. The removal of Zn^{2+} and Cd^{2+} at different pH, contact time, elution solution and interfering ions was investigated. Kim et al. [83] performed an experiment for the removal of Cu^{2+} using suspended anatase-type titanium dioxide nanoadsorbents. The adsorption amount increased rapidly with an increasing solution pH and temperature. The obtained adsorption equilibrium constant (K_{ads}) was 0.854 and adsorption isotherm of Cu^{2+} adsorption fitted well to Langmuir adsorption isotherm. Skubal et al. (2002) reported removal of aqueous Cd^{2+} from waste water using TiO_2 nanoadsorbents [86]. More than 90% of Cd^{2+} was removed by both adsorption and reduction processes onto the TLA-modified TiO_2. These removal and reduction processes were catalytic in nature.

3.4.2.3 Nanosized Cerium Oxides

Nano cerium oxides (CeO_2) have been explored as the excellent nanoadsorbents for heavy metals removal from water due to specific surface area, less toxicity, good catalytic activity [87], blue shift in absorption spectra [88], lattice expansion [88], phase transformation [89], and photovoltaic response [90]. Cao et al. [91] developed, hollow ceria nanospheres via microwave assisted hydrothermal method. These ceria hollow nanospheres then were examined for the removal of As^{5+} and Cr^{6+} from water. The obtained maximum adsorption capacity for As^{5+} is 22.4 mg/g and 15.4 mg/g Cr^{6+}, and these values were extremely higher than other ceria nanostructures reported in data. Recillas et al. [92] investigated suspended CeO_2 NPs stabilized with hexamethylenetetramine and used for the removal of dissolved chromium (VI) from water. Several concentrations of adsorbent and adsorbate were tested, trying to cover a large range of possible real conditions. These results can be used to propose this treatment sequence for a clean and simple removal of drinking water or wastewater reuse when a high toxicity heavy metal such as Cr^{6+} is responsible for water pollution. Di et al. [93] synthesized CeO_2 NPs supported on aligned carbon nanotubes (ACNTs) nanoadsorbents and investigated these for the removal of Cr^{6+} from drinking water. The result indicated that CeO_2/ACNTs nanoadsorbents show excellent adsorption of Cr^{6+} and the maximum adsorption capacity obtained as 30.2 mg/g. These studies put forward that CeO_2/ACNTs have enormous prospective applications in water treatment.

Haron et al. [94] developed cerium modified zeolite P (CeZP) nanoadsorbents and used these for the removal of As^{5+} from aqueous solution. The sorption capacity increased with increasing temperature 25–90 °C. The adsorption of As^{5+} onto CeZP follows Langmuir model and the obtained maximum sorption capacity was 8.72 mg/g (25 °C) and increased to 23.42 mg/g (90 °C), indicating an endothermic process. The results show that nanoadsorbents' CeZP has excellent removal efficiency of As^{5+} from wastewater (wood treatment industry).

3.4.2.4 Nanosized Magnesium Oxides

Recently, numerous works have focused on the synthesis of nanosized magnesium oxides (MgO) of various morphologies for the removal of heavy metals from water. Gao et al. (2008) reported a facile method to fabricate MgO of different morphologies and investigated their influence on the removal of Cr^{6+} and the result indicates excellent adsorption of Cr^{6+}. Also the flowerlike morphology of mesoporous MgO was synthesized and investigated for the adsorption capabilities of Cd^{2+} and Pb^{2+} [95]. The concentration of Cd^{2+} and Pb^{2+} decreased from 100 to 0.007 and 0.05 mg/L, respectively (at equilibrium time: 120 min). It shows that removal of Cd^{2+} and Pb^{2+} using flowerlike MgO was much lower than the Pollutant Dischargeable Standard in China ($Cd^{2+} < 0.01$ mg/L, $Pb^{2+} < 0.1$ mg/L). Koivula et al. [96] reported the used of Cryptomelane type MnO for the removal of Cu^{2+} from wastewaters. The cryptomelane has ion exchange properties for weak acidic ion exchangers that show high-quality selectivity toward transition metals. This shows obtained capacity of 1.3 m mol/g for Cu^{2+} and distribution coefficient as high as $\sim 10^4$ ml/g, promising future application for the removal of metal ions from water. Pakarinen et al. [97] reported two tunnel-structured oxides of nanoporous manganese oxides (OMS-1 and OMS-2) using hydrothermal method for the removal of metals ions and acid using kinetic measurements at different metal ion concentrations. This results show that OMS materials selectively adsorb Cu^{2+}, Ni^{2+}, and Cd^{2+} in the presence of Ca and Mg. The study shows that both the nanoadsorbents were stable and their maximum Cu^{2+} uptake capacity was obtained as 0.9–1.3 m mol/g.

3.4.2.5 Nanosized Aluminum Oxides

Recently, alumina (Al_2O_3) has been explored as the adsorbent for heavy metals, and α-Al_2O_3 is anticipated to be more adsorptive active than Al_2O_3 [98–100]. Its chemical or physical modification of γ-Al_2O_3 nanoparticles with certain functional groups shows donor atoms such as oxygen, nitrogen, sulfur, and phosphorus and is expected to improve their sorption toward heavy metals [100, 101]. Fan et al. [102] reported hydrous amorphous nanoadsorbents Al (HAO), Fe (HFO), and Mn (HMO) oxides show high affinity for heavy metal ions. These nanoadsorbents then have been investigated for the removal of Pb^{2+} from water, the results show excellent removal efficiency. Pu et al. [103] reported fixing γ-mercaptopropyltrimethoxysilane (γ-MPTMS) on the surface of γ-Al_2O_3 improve its selectivity toward Cu, Hg, Au, and Pd ions rather than other ions. The mechanism responsible for the selectivity adsorption of metal ions was through the affinity of -SH group, the hydrolyzation of metal ions, and electrostatic adsorption. The result shows the obtained adsorption capacity of modified γ-Al_2O_3 nanoadsorbents were found as 10.4, 16.3, 15.3, and 17.4 mg/g for Hg, Cu, Au, and Pd, respectively. Furthermore, Afkhami et al. [104] reported nanoγ-Al_2O_3-coated sodium dodecyl sulfate modified with 2, 4-dinitrophenylhydrazine (DNPH) was used as adsorbent for removal of heavy metals Pb^{2+}, Cr^{3+}, Cd^{2+}, Ni^{2+}, Co^{2+}, and Mn^{2+}. The result indicates that Freundlich isotherms sorption model fitted well for the adsorption of Mn^{2+}, Pb^{2+}, Cr^{3+}, and Cd^{2+}, ions whereas, Langmuir model fitted well for Ni^{2+} and Co^{2+} ions. The obtained maximum Langmuir adsorption capacity values for Pb^{2+}, Cr^{3+}, and Cd^{2+} ions were 100, 83.33 and 100 mg/g, respectively. Table 3.5 shows various nanoadsorbents for the removal of heavy metals/metalloids from water.

Table 3.5 Comparison of various nanoadsorbents used for aqueous Pb^{2+} remediation

Nanoadsorbents	Heavy metals	References
Fe_3O_4	Pb^{2+}	[74]
Water-soluble Fe_3O_4	Pb^{2+} and Cr^{6+}	[75]
AF-Fe_3O_4	Pb^{2+}, Cd^{2+} and Cu^{2+}	[76]
Fe_3O_4/HA	Hg^{2+}, Pb^{2+}, Cd^{2+} and Cu^{2+}	[77]
Monodisperse Fe_3O_4	Pb^{2+}	[78]
α-FeOOH	Cu^{2+}	[79]
Goethite and hematite (α- Fe_2O_3)	Cu^{2+}	[80]
γ-Fe_2O_3	Cr^{6+}	[81]
γ-Fe_2O_3	Cr^{6+}, Cu^{2+} and Ni^{2+}	[82]
TiO_2	Pb, Cd, Cu, Zn, and Ni	[45]
TiO_2, NPs	Zu^{2+}, Cd^{2+}	[85]
Anatase-type TiO_2	Cu^{2+}	[83]
Acid-modified TiO_2	Cd^{2+}	[86]
Hollow nanospheres CeO_2	As^{5+} and Cr^{6+}	[91]
CeO_2	Cr^{6+}	[92]
CeO_2/ACNTs	Cr^{6+}	[93]
CeZP	As^{5+}	[94]
Mesoporous flowerlike MgO	Cr^{6+}, Cd^{2+}, Pb^{2+}	[95]
Cryptomelane type MnO	Cu^{2+}	[96]
OMS-1 and OMS-2	Cu^{2+}, Ni^{2+} and Cd^{2+}	[97]
Hydrous amorphous Al oxides	Pb^{2+}	[102]
γ-MPTMS modified γ-Al_2O_3	Cu^{2+}, Hg^{2+} and Pb^{2+}	[103]
DNPH modified γ-Al_2O_3	Pb^{2+}, Cd^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+} and Mn^{2+}	[104]

3.5 Polymer and Amino Acid Supported Nanomaterials for Heavy Metals/Metalloid

The fast adsorption and high uptake of heavy metals of nanoadsorbents mainly depend on functional groups and large surface area [47, 105]. Metal and metal oxide and carbon-based nanomaterials have high surface area but don't have to adsorb functional group. To overcome these problems, organic polymer, polyphenylenediamine, holds a large amount of polyfunctional groups (amino and imino groups) can effectively adsorb heavy metal ions, whereas their small specific area and low adsorption rate limit their application [47]. Therefore, new sorbents with both polyfunctional groups and high surface area are still expected. The development of hybrid sorbents has opened up the new opportunities of their application in fast removal of heavy metals from water [47, 106]. Chen et al. [107] prepared magnetite coated 3-aminopropyl trimethoxysilane (APTES). Then, the modified nanoparticles further grated by different heterocyclic groups (HCG) (Fe_3O_4@SiO_2-NH-HCGs). This Fe_3O_4@SiO_2-NH-HCGs were used for the removal of heavy metal cations such as Cu^{2+}, Hg^{2+}, Pb^{2+}, and Cd^{2+}. The result shows 96% removal of heavy metals within 20 min at normal temperature and has good stability and reusability.

Huang and Chen [108] investigated magnetic nanoadsorbent by the covalent binding of polyacrylic acid (PAA) on the surface of Fe_3O_4 nanoparticles and then followed amino-functionalization using diethylenetriamine (DETA) via carbodiimide activation. This amino-functionalized magnetic nano-adsorbent shows excellent capability for the rapid and efficient adsorption of metal cations and anions from aqueous solutions via the chelation or ion exchange mechanisms. The maximum adsorption capacities and Langmuir adsorption constants were 12.43 mg/g and 0.06 L/mg for Cu^{2+} and 11.24 mg/g and 0.0165 L/mg for Cr^{6+}, respectively.

Cai et al. [109] used polyacrylic acid stabilized amorphous calcium carbonate nanoparticles and used it for the application of heavy metal removal from water. The maximum removal capacities for Cd^{2+}, Pb^{2+}, Cr^{3+}, Fe^{3+}, and Ni^{2+} ions were found to be 514.62, 1028.21, 258.85, 320.5, and 537.2 mg/g, respectively.

Pavlidou and Papaspyrides [110] reported a review on recent advances in the field of polymer-layered silicate nanocomposite. These nanocomposites have attracted both academic and industrial attention because they exhibited dramatic improvement in properties at very low filler contents.

Liu et al. [111] reported hybrid polymers from the ring-opening polymerization of pyromellitic acid dianhydride (PMDA) and phenylaminomethyl trimethoxysilane (PAMTMS) and used it for the removal of Cu^{2+} and Pb^{2+} from water. The result indicates excellent removal efficiency due to novel size and shape dependent properties of nanoparticles. Table 3.6 shows the polymer-based nanoadsorbents.

Table 3.6 Polymer and amino acid supported nanoadsorbents for heavy metal removal from water

Polymer and amino acid supported nanoadsorbents	Heavy metals	References
Fe_3O_4@SiO_2-NH-HCGs	Cu^{2+}, Hg^{2+}, Pb^{2+} and Cd^{2+}	[107]
PAA coated Fe_3O_4	Cu^{2+} and Cr^{6+}	[108]
Polyacrylic Acid Stabilized Amorphous Calcium Carbonate Nanoparticles (ACC)	Cd^{2+}, Pb^{2+}, Cr^{3+}, Fe^{3+} and Ni^{2+}	[109]
Hybrid polymers from the ring-opening polymerization of PMDA and PAMTMS	Cu^{2+} and Pb^{2+}	[111]

3.6 Conclusion

Recent development in nanotechnology has provided much more opportunities to develop nontoxic, cost-effective and environmentally friendly water treatment technology. Nanomaterials have blessed with a numerous numbers of physico-chemical properties that make them attractive for wastewater purification. Many researchers have investigated nanomaterials as sorbents and reported that it is best tools for heavy metal removal, due to their small size unique structure and surface modification. These nanomaterials rapidly remove heavy metals/metalloids ions even at low concentration, with high selectivity and adsorption capacity. The exploitation of new efficient adsorption materials is essential and will continue infinitely, the future of nanomaterials in removal heavy metal ions in wastewater treatment is fairly bright.

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